

Measurements and relation between the dynamic and static interactions between surfaces separated by thin liquid and polymer films

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Abstract - Two techniques are described for measuring the shear viscosities of thin liquid films confined between two molecularly smooth solid surfaces. Both techniques employ the Surface Forces Apparatus which has already been extensively used to measure the static, *i.e.*, equilibrium, interactions between surfaces in liquids. With one or other of the new dynamic techniques shear viscosities of the confined liquids can be directly measured as a function of film thickness with a precision of about 0.1 nm. In particular, the techniques allow for the determination of the location of the non-slip plane (or *shear plane*, or *hydrodynamic layer thickness*) to similar accuracy. One of the techniques is more suitable at low shear rates ($<10^3 \text{ s}^{-1}$), the other at high shear rates (up to $>10^6 \text{ s}^{-1}$). Results are presented for measurements made on a variety of simple liquids and polymer systems. It is found that for simple liquids such as organic liquids and water between two mica surfaces the viscosity of the film is the same (within 10%) as that expected from the bulk liquid viscosity down to film thicknesses as small as ten molecular diameters (of the liquid molecules). This implies that the shear plane is effectively located at the solid-liquid interface within a few ångströms, *i.e.*, well within one molecular diameter of the surface (again, so long as the film thickness is greater than about ten molecular diameters). With the polymer systems (both pure polymer melts and polymers adsorbed from solution) it is found that the shear plane is effectively located at (1-2) R_g away from the solid-liquid interface (where R_g is the unperturbed radius of gyration of the polymer). Further, unlike the case of simple liquids which show no deviations from purely Newtonian behavior even at shear rates above 10^5 s^{-1} , significant deviations are seen in the polymer melt systems in submicron films already at shear rates of $\sim 10^3 \text{ s}^{-1}$. An attempt is made to correlate the dynamic results with the static intersurface forces previously measured on these systems.

INTRODUCTION

A knowledge of the viscosity of both simple liquids and polymer fluids in thin films between two surfaces or near one surface is important for understanding many dynamic and rheological phenomena, such as the rheological behavior of concentrated colloidal dispersions, the drainage of thin films, in lubrication, in determining coagulation rates, and in calculating the diffusion and flow of liquids in confined spaces such as small pores and capillaries. Of particular interest is the determination of the position of the non-slip plane, or shear plane, or - for polymer systems - the hydrodynamic layer thickness in such systems, and especially for interpreting the results of various dynamic experiments, *e.g.*, light scattering and neutron scattering of dispersed systems.

The hydrodynamic thickness Δ_H of a variety of polymer layers adsorbed from solution have previously been measured using capillary viscometers (refs. 1,2) and sintered glass disc viscometers (ref. 3), and more recently by quasielastic light scattering (ref. 4), photon correlation spectroscopy (ref. 5) and using the dynamic surface forces apparatus (refs. 6-11). An excellent review up to 1982 is given in ref. 12. The results on a variety of different surface adsorbed polymer systems all showed that at saturation adsorption Δ_H values are

typically between one and two radii of gyration - the higher values being obtained in θ or better than θ conditions (good solvents). These results appear to agree very well with various theoretical analyses (refs. 5,13) which predict $\Delta_H \propto \sqrt{M_w}$ in general, and $\Delta_H \approx 2R_g$ for high molecular weight polymers adsorbing from θ -solvents. Lower values for Δ_H are expected in worse than θ conditions and higher values in better than θ conditions as is indeed found experimentally (refs. 4, 8,12-15).

The aim of this work was to extend these measurements to pure polymer liquids (polymer melts), including linear chain hydrocarbon liquids (alkanes, or liquid paraffins), and even simple spherical molecules, in order to establish whether the values of Δ_H in such systems also scale with R_g , or with some other property of the liquid. Finally, an attempt is made to correlate these dynamic results on Δ_H with (i) the equilibrium "steric" forces measured in such systems and (ii) the conformation (structure) of the liquid molecules at the interfaces.

EXPERIMENTAL TECHNIQUES AND RESULTS

The surface forces apparatus for static force measurements

The Surface Forces Apparatus has been much described in the literature (refs. 16,17) where it has been mainly used to measure the static, or equilibrium, force-laws (i.e., the force, F , as a function of separation, D) between molecularly smooth cylindrical surfaces in liquids. The surfaces are moved by a combination of a mechanical micrometer (coarse control to $\pm 1\mu\text{m}$), a differential spring (medium control to $\pm 10\text{\AA}$), and a piezoelectric ceramic tube (fine control to $\pm 1\text{\AA}$), while the surface separation is measured to within $\pm 1\text{\AA}$ by an optical technique using *fringes of equal chromatic order*. The movement (and any deformations) of these curved fringes provide direct quantitative information on the relative motion (and any force-induced shape changes) of the two interacting surfaces. The intersurface force is measured from the deflection of a double-cantilever force-measuring spring supporting the lower surface. The apparatus was recently modified (refs. 6-11) to enable various dynamic interactions to be studied, two of which will now be described.

Dynamic measurements

Two new dynamic techniques were recently developed (refs. 7,11) for directly measuring the *viscosity profiles* (viscosity as a function of distance) across very thin liquid films between the two curved surfaces, providing information such as the position of the shear plane relative to $D = 0$ (or Δ_H), non-Newtonian behavior at high shear rates, etc. Both techniques involve applying an AC voltage to the piezoelectric tube supporting the upper surface, causing it to vibrate at frequency ν and amplitude A_0 . The viscous coupling due to the liquid between the two surfaces induces the lower surface to vibrate at the same frequency ν but with amplitude A_x ($< A_0$) and phase ϕ relative to the upper surface. The amplitude of oscillation of the intersurface separation D is therefore given by $A_D = |A_0 - A_x e^{i\phi}|$. Concerning the equations of motion these have been solved in a number of previous papers (refs. 6,7,9,11). If D is the mean distance of separation between the two surfaces then the shear viscosity of the liquid in the gap is given by either of the following equations.

$$\eta = \frac{K(1-\nu^2/\nu_0^2)D}{12\pi^2 R^2 \nu} \left[\left(\frac{A_0}{A_D} \right)^2 - 1 \right]^{1/2} \quad (1)$$

and

$$\eta = \frac{K(1-\nu^2/\nu_0^2)D}{12\pi^2 R^2 \nu \tan\phi} \quad (2)$$

where R is the radius of curvature of the two curved (crossed cylindrical) surfaces, K the stiffness of the spring supporting the lower surface (the force-measuring spring), and ν_0 the natural resonance frequency of the lower support. The above equations are valid for small amplitudes A_D relative to D ($A_D < 0.15D$).

For driving frequencies ν below about 3 Hz (low shear rates) the movement of the interference fringe pattern (and hence the surfaces) can be monitored with a video camera and recorded on a video-cassette recorder. The recorded data is later analyzed, and provides all the necessary information (such as the amplitude of oscillations A_0 and A_D , the mean intersurface separation D , the radius of the surfaces R , and the frequency ν) needed to compute the viscosity of the liquid using Eq. (1). However, due to the 50 frames/sec recording speed of the cassette recorder, this method is suitable only at low shear rates or, more specifically, low frequencies ($\nu < 3$ Hz and $\nu \ll \nu_0$) where the recorded fringes remain sharp.

Thus, using this method for a Newtonian liquid, a plot of $12\pi^2 R^2 \eta \nu / K[(A_0/A_D)^2 - 1]^{1/2}$ against D should be a straight line of unit slope passing through the origin at $D = 0$ (if $\Delta_H = 0$) or passing through the D -axis at a finite distance of $D = 2\Delta_H$ (where Δ_H is the hydrodynamic layer thickness *per surface*).

The second method is similar to the first except that the metal spring normally supporting the lower surface (see ref. 17, Fig. 1) is replaced by a piezoelectric *bimorph* strip (Fig. 1) which acts both as a spring and as a displacement strain gauge (a clamped bimorph develops a voltage across its exposed surfaces proportional to the displacement of the free end). By feeding the input AC voltage to the piezoelectric tube supporting the upper surface and the output voltage from the bimorph into a lock-in amplifier, the phase ϕ of the lower surface can be measured, while the surface separation D is still measured from the optical fringes.

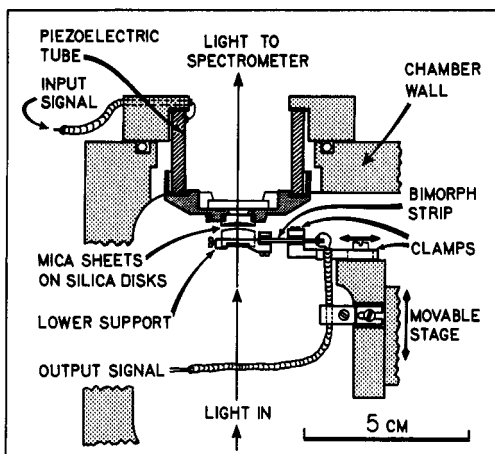


Fig. 1. Modifications to the basic Surface Forces Apparatus (refs. 16,17) for making high frequency (high shear-rate) dynamic measurements using the bimorph-lock-in amplifier method, the results of which are shown by the dashed curves in Fig. 2.

To interpret the data of this method we use Eq. (2) which shows that for a Newtonian liquid a plot of $12\pi^2 R^2 \eta \nu \tan \phi / K[1 - \nu^2/\nu_0^2]$ against D should yield a straight line of unit slope and where again the effective position of the shear plane is given by the intercept of this line extrapolated through the distance axis. This second dynamic method is not limited to low frequencies (as is the first method) and is therefore particularly suitable for high shear-rate high-frequency measurements. In addition, with the bimorph-lock-in amplifier system of this method one can make accurate measurements even at very small amplitudes of vibration, of order 1\AA or less, which is well beyond the resolution attainable with the video-camera-recorder system of the first method. The first method, however, is definitely preferable at low frequencies, below 5 Hz, where the performance of lock-in amplifiers rapidly deteriorates.

Materials

Concerning pure one-component liquid systems, results will be shown for the simple liquids, cyclohexane (C_6H_{12}) and water, for *n*-tetradecane ($C_{14}H_{30}$), and for three polymer melts consisting of linear chain molecules with 20-65 segments, n . These are: polydimethylsiloxane (PDMS) with $M_w \approx 3,700$, $n = 50$, and $R_g \approx 16\text{\AA}$; polybutadiene I (PB I) with $M_w \approx 1,000$, $n = 20$, and $R_g \approx 12\text{\AA}$; and PB II with $M_w \approx 3,500$, $n = 65$, and $R_g \approx 22\text{\AA}$. Finally, results will also be shown for a system of polystyrene ($M_w \approx 900,000$, $R_g \approx 260\text{\AA}$) adsorbed from cyclohexane at slightly below the θ -temperature.

Results

Figure 2 shows plots of the results obtained for the seven liquid systems described above. The left-hand ordinate gives results obtained using the video-camera-recorder system of the first method (solid lines); the right-hand ordinate is for results using the bimorph-lock-in amplifier system of Fig. 1 (dashed lines).

First we note that for the three simple liquids, cyclohexane, tetradecane and water their lines coincide (lines A) and have unit slope. These lines, when extrapolated below about ten molecular diameters, pass through the origin (at $D = 0$) within a few ångströms. This indicates that these liquids retain their bulk (continuum) viscous properties even in films as thin as 10 molecular diameters, and that the shear plane is at $D = 0$ (*i.e.*, $\Delta_H = 0$) even at the highest shear rates studied (dashed line A, which is for *n*-tetradecane, measured at a frequency of $\nu = 200$ Hz and at a maximum shear rate of $\sim 2 \times 10^5$ s⁻¹).

By contrast, the three polymer melts and the polystyrene-in-cyclohexane sample all yield straight lines of unit slope at separations beyond about 5 R_g (indicating bulk viscous properties), but the lines are shifted outward so that on extrapolation they cut the D -axis at $D = 2\Delta_H$, where the hydrodynamic layer thickness Δ_H for these four samples are as follows

	R_g (Å)	Δ_H (Å)
PB I (melt)	12	30
PDMS (melt)	16	30
PB II (melt)	22	40
PS/cyclohexane	260	260

We note that in general the values of Δ_H are in the range (1 - 2) R_g . In particular, for the polystyrene in cyclohexane system the measurements were made in worse than θ conditions, *i.e.*, at 26°C whereas $T_\theta = 35^\circ\text{C}$, which may be the reason why the value of Δ_H was the lowest measured in comparison to R_g , *viz.* $\Delta_H \approx R_g$. By contrast, for the pure polymer melt systems where the adsorbed segments may be considered to interact in a θ -solvent the values of Δ_H were closer to $2R_g$, consistent with theoretical expectations for such systems (refs. 5,13).

Preliminary measurements with polymers at high shear-rates using the bimorph-lock-in amplifier method (dashed lines in Fig. 2 inset) show that for the polymer melt PB I deviations occur at driving frequencies above about 10 Hz, corresponding to maximum shear rates above $\sim 10^3$ s⁻¹. These deviations become more marked at higher frequencies and are characterized by an effectively increased viscosity at small surface separations which cannot be explained simply in terms of a shift in the position of the shear plane or an increasing Δ_H . They appear to herald some non-Newtonian behavior in submicron polymer films whose origin is as yet unknown.

DISCUSSION AND CONCLUSIONS

The results reported here and in previous papers (refs. 7,8) show that for simple liquids including linear chain molecules such as alkanes with up to $n = 14$ segments their viscosity in thin films is the same, within 10%, as the bulk even for films as thin as ten molecular diameters (or segment widths). This also implies that the shear plane is effectively at the solid liquid interface within one molecular diameter, and these conclusions remain valid even at the highest shear rates studied (of $\sim 2 \times 10^5$ s⁻¹). By contrast, for a variety of polymer systems including polymer melts with $n > 20$ and high molecular weight polymers adsorbed from solution the shear plane is located at $D = \Delta_H = (1-2)R_g$ from the solid-liquid interface, manifesting itself as an effectively immobilized layer of thickness Δ_H at each surface. This is in agreement with various theoretical analyses (refs 5,13) which predict that $\Delta_H \approx 2R_g$ under θ -conditions. Since for the three polymer melt systems it was indeed found that $\Delta_H \approx 2R_g$ at low shear rates ($< 10^3$ s⁻¹) we may conclude that, as far as the hydrodynamic interactions of polymer melts are concerned, (i) they interact as if those molecules in contact with the surfaces are effectively

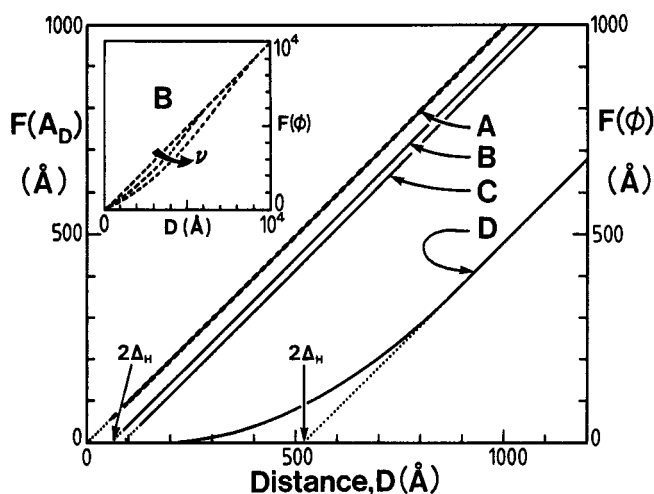


Fig. 2. Left-hand ordinate (solid lines): Plot of $F(A_D) = 12\pi^2 R^2 \eta \nu / K [(A_0/A_D)^2 - 1]^{1/2}$ against surface separation D , based on Eq. (1) using the video-camera-recorder method suitable for low shear rates (low frequencies $\nu < 3$ Hz). Right-hand ordinate (dashed lines): Plot of $F(\phi) = 12\pi^2 R^2 \eta \nu \tan\phi / K [1 - \nu^2/\nu_0^2]$ against D , based on Eq. (2) using the bimorph-lock-in amplifier method (Fig. 1) suitable for high shear rates (high frequencies $\nu > 2$ Hz). In each case the inverse slope of the line is equal to $\eta_{\text{eff}}/\eta_{\text{bulk}}$ where η_{eff} is the effective viscosity of the liquid in the gap, and where the dotted extrapolated lines cut the D -axis at $D = 2\Delta_H$, where Δ_H is the effective hydrodynamic layer thickness per surface.

- Curve A: Results (refs. 7,8,23) for cyclohexane, water and tetradecane (up to frequencies of $\nu = 200$ Hz).
- Curve B: Results (ref. 10,11) for polybutadiene, PB I ($R_g \approx 12\text{\AA}$), and polydimethylsiloxane, PDMS ($R_g \approx 16\text{\AA}$), which are almost identical those of PB I.
- Curve C: Results (ref. 11) for PB II ($R_g \approx 22\text{\AA}$). The data of curves A, B and C were all taken at 22°C .
- Curve D: Results (ref. 8) for polystyrene ($M_w \approx 900,000$, $R_g \approx 260\text{\AA}$, $T_\theta \approx 35^\circ\text{C}$) adsorbed to saturation from a $12 \mu\text{m}/\text{ml}$ cyclohexane solution, measured at 26°C . The bulk viscosity of this dilute solution is practically indistinguishable from that of pure cyclohexane.
- Inset: Results (ref. 11) for PB I (curve B) showing deviations from purely Newtonian behavior at progressively higher driving frequencies ν above 10 Hz.

"adsorbed" or *pinned* to the surfaces, at least during the time scale of the measurements (this may not be true for the *static* or equilibrium interactions), and (ii) the "adsorbed" polymers interact as if surrounded by a θ -solvent.

Only in the case of the interactions of polystyrene adsorbed from cyclohexane (ref. 8) was the value of Δ_H significantly lower, *viz.* $\Delta_H \approx R_g$ rather than $\Delta_H \approx 2R_g$. This finding is very reasonable, and perhaps to be expected, since the interaction occurred in worse than θ -conditions, *i.e.*, at about 9°C below the θ temperature of 35°C .

These conclusions, obtained from the dynamic experiments, appear to correlate very nicely with those obtained from static force measurements where it has been established that for the interactions of adsorbed polymers from solution the range of the "steric" forces increases with the increasing goodness of the solvent - increasing from about $2R_g$ to $(6-8)R_g$ as the temperature changes from a few degrees below T_θ to above T_θ (refs. 18,19). This latter range is exactly the same as that found in pure polymer melt systems (refs. 9,10,20), which again points to at least a qualitative similarity in the interactions of two surfaces across polymer melts with those between surfaces with adsorbed polymers in a θ -solvent (or in good solvents).

At small surface separations, below a few R_g , or below about 10 segment diameters, there is evidence that both the static and dynamic interactions in polymer systems become quite complicated (refs. 9,10,20,21; and see curve D in Fig. 2). For the case of alkanes and polymer melts there are strong indications that the close approach of two surfaces forces the molecules to orient parallel to the surfaces (refs. 10,20,22,23), which leads to an oscillatory force or to a steep repulsion between the surfaces at separations below about 30Å.

In the case of adsorbed high molecular weight polymer layers (ref. 21), such as polystyrene adsorbed from cyclohexane, the exact conformation of the highly compressed polymer is not known, though the steep repulsion at small separations ($D < R_g$) suggests a transition to the glassy state. Likewise, there are as yet no theories to explain the viscosity profile at small separations (cf. Fig. 2, curve D at separations below 750Å), which can no longer be described simply in terms of an immobilized layer or a simple shift in the shear plane.

Clearly, more research is needed, both experimental and theoretical (e.g., using Monte Carlo or Molecular Dynamics simulations), in order to elucidate the structure and the static and dynamic interactions of polymers in very thin films, and of the correlations between them.

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